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Jerry Boatz (PRSP) et al., "First Principles Calculation of the Chemisorption Properties of Nitro-
containing Molecules on the Al(111) Surface (Multiscale Simulations of High Energy Density Materials
Challenge Project)"

    DoD Users Group Conference   **(Statement A)**
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First Principles Calculation of the Chemisorption Properties of Nitro-containing Molecules on the Al (111) Surface
(Multiscale Simulations of High Energy Density Materials Challenge Project)

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ABSTRACT

First-principles calculations based on spin-polarized density functional theory (DFT) and the generalized gradient approximation (GGA) have been used to study the adsorption of nitromethane (NM), 1,1-diamino-2,2-dinitroethylene (FOX7) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) on Al(111) surface. The calculations employ aluminum slab geometries and 3D periodic boundary conditions. Three surface models have been considered in these studies. The first model corresponding to $\left(\sqrt{7} \times \sqrt{7}\right) R 19.1°$ surface reconstruction has been used for the case of nitromethane. In the case of the larger molecular systems FOX7 and HMX, a slab model containing 3x3 and respectively 4x4 surface units cells have been employed. Based on these calculations we have determined that both dissociative and nondissociative adsorption mechanisms are possible depending on the molecular orientation and the particular surface sites involved. N-O bond dissociation occurs when molecular adsorption takes place with the nitro groups oriented toward the surface. The dissociated oxygen atom forms strong Al-O bonds with the neighbor Al sites around the dissociation sites. Additionally, the radical species obtained as a result of oxygen atom elimination remain bonded to the surface. In some instances, both oxygen atoms in the nitro group dissociate and oxidize the aluminum surface. Finally, for the case of nondissociative adsorption, various N-O-Al bridge-type bonding configurations can be formed. Based on the data provided from these studies it can be concluded that oxidation of the aluminum surface readily occurs, either by partial or complete dissociation of the oxygen atoms from the NO$_2$ group.

I. Introduction

Powderized aluminum has long been used as an energetic ingredient in rocket propellant formulations, comprising approximately 15-20% of conventional ammonium perchlorate solid propellant.[1] However, the performance of aluminum is reduced by the rapid formation of an aluminum oxide overcoat on aluminum particles prior to combustion, which also inhibits efficient burning. Furthermore, formation of the oxide overcoat severely reduces the potential advantages of using high surface-to-volume-ratio ultrafine aluminum particles, which would otherwise have highly desirable properties such as enhanced burn rates.

In order to inhibit the rapid formation of an oxide overcoat on the ultrafine aluminum particles without simultaneously degrading performance, it has been proposed to coat the aluminum particles with an energetic material such as RDX. In order to clarify some of the fundamental issues related to the deposition of energetic materials on aluminum nanoparticles, the present work focuses on obtaining an atomic-level description of the interactions between various energetic compounds such as nitromethane (NM), 1,1-diamino-2,2-dinitroethylene (FOX-7), and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclo-octane (HMX) with an aluminum surface. Specifically, first-principles quantum chemical calculations were used to determine if different nitro-containing compounds of interest for energetic materials applications would effectively inhibit the formation of an oxide overcoat on the surface of aluminum.

II. Computational Methods

Spin-polarized generalized gradient approximation (GGA) density functional theory, using ultrasoft Vanderbilt-type pseudopotentials[2,3] and the PW91 exchange-correlation functional[4] have been used to optimize the geometries of the energetic molecules NM, FOX-7 and HMX adsorbed on Al(111) surface. Periodic boundary conditions were used, with the one electron pseudo-orbitals expanded over a plane wave basis set

$$\partial_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{G}} \exp(i\mathbf{G}\mathbf{r}) . \tag{1}$$

The expansion includes all plane waves whose kinetic energy is less than a predetermined cutoff energy E_{cut}, i.e., $\square^2 G^2/2m < E_{cut}$, where E_{cut} = 396 eV. The k-points are obtained from the Monkhorst-Pack scheme.[5]

The Al surface has been represented by the aid of a slab model with periodic boundary conditions applied in all three directions. In order to decrease the computational load slabs of different sizes have been used for specific systems. Particularly, a $\left(\sqrt{7} \times \sqrt{7}\right)$R19.1° supercell with four layers and containing 28 Al atoms has been used to study NM adsorption. For the larger molecules FOX7 and HMX we have used a 3x3 and 4x4 surface model, respectively, containing 36 and 48 Al atoms, respectively. All calculations have been done using the ab initio total-energy program VASP (Vienna *ab initio* simulation program).[6]

III. Results and Discussion

The adsorption of nitromethane (which is a prototype for larger energetic molecules such as RDX, HMX, and FOX-7) on the Al(111) surface was examined in detail for five distinct orientations of NM relative to the metallic surface. The corresponding configurations are depicted in panels (a)-(e), respectively, in Figure 1. Panels (a) – (c) show three different initial orientations of the NM molecule in which the C-N bond is perpendicular to the surface with the nitro group pointing down toward the surface. The final (i.e., optimized) configuration in panel (a) illustrates marked distortions of the nitro group due to the strong interactions of the oxygen atoms with the aluminum surface. In panel (b), one of the oxygen atoms is completely dissociated from the nitro group and is bound to two neighboring Al atoms. However, the NM fragment also strongly chemisorbs on the surface, forming bonds to aluminum via both the nitrogen atom and the remaining oxygen atom. In the optimized configuration shown in panel (c), both oxygen atoms are completely dissociated from the nitro group and form strong bonds to the surface. Likewise, the nitrogen atom in the original nitro group also forms a bond to the

metal surface.

Panel (d) in Figure 1 shows a configuration in which the C-N bond of nitromethane originally is parallel to the metallic surface. In the final configuration, however, rotation of NM has occurred in order to maximize the interactions of the nitro group with aluminum. The final geometry is similar to that in panel (b), in that one of the oxygen atoms is completely dissociated from the nitro group. Additionally, the resulting NM fragment is also strongly chemisorbed on the surface via bonds with the nitrogen atom and the remaining oxygen atom.

An orientation in which the NM molecule initially is perpendicular to the metallic surface, but with the methyl group pointing toward the surface, is shown in panel (e) in Figure 1. In this case chemisorption does not occur since the methyl group does not strongly interact with the surface aluminum atoms.

Figure 2 shows two sets of initial and final configurations of the FOX-7 molecule (1,1-diamino-2,2-dinitroethylene) interacting with the aluminum (111) surface. In panel (a), the approximately planar FOX-7 molecule is initially perpendicular to, with one of the nitro groups pointing toward, the aluminum surface. As seen in the final configuration in panel (a), one of the oxygen atoms is completely dissociated from FOX-7. Furthermore, another two oxygen atoms and one of the nitrogen atoms form strong bonds to surface aluminum atoms. Panel (b) in Figure 2 shows an initial configuration in which the FOX-7 molecule is parallel to the surface. In contrast to nitromethane, which reorients from a parallel to a perpendicular orientation (panel (c) in Figure 1), the FOX-7 molecule remains parallel to the aluminum surface in the final configuration. Nonetheless, each of the four oxygen atoms forms strong bonds to the surface, although dissociation of oxygen does not take place.

Finally, Figure 3 shows initial and optimized structures of HMX on the aluminum (111) surface. In the optimized orientation, an oxygen atom from one of the original nitro groups is completely dissociated from HMX and is chemisorbed onto the surface. A second oxygen atom also chemisorbs to a surface aluminum atom, although it remains bonded to a nitrogen atom in HMX.

IV. Summary and Conclusions

The structures of NM, FOX-7, and HMX interacting with slab models of Al (111) surface have been optimized using spin-polarized GGA plane-wave basis density functional theory in order to investigate possible reaction mechanisms at the molecule-metallic surface interface. Energetic compounds containing the relatively weak nitramine ($N-NO_2$) and relatively strong $C-NO_2$ linkages were examined. Preliminary predictions of the interactions between the energetic molecules NM, HMX and FOX7 have indicated a common propensity for oxidation of the aluminum surface by the oxygen-rich nitro groups (NO_2) present in these molecules. Dissociation of the nitro groups and formation of strong Al-O bonds appears to be a common mechanism for these molecules. These results suggest that nitro-containing energetic compounds are not likely to be effective coating materials for preventing rapid oxidation of aluminum.

Future work will extend this set of investigations to first principles density functional theory

calculations of the interactions of several ionic systems such as ammonium nitrate or ammonium dinitramide with an Al surface. In these investigations, key reaction pathways of these energetic salts on an aluminum surface will be computed. We will furthermore attempt to understand the type of chemical processes that can take place at the interface of aluminum hydrides with different classes of energetic materials. In this case we will focus on the case of ammonium nitrate and RDX crystals where the detonation properties are significantly affected by the interaction with aluminum hydrides. Additional future areas may include studies of the interactions of nitrate esters (C-O-NO$_2$) with aluminum.

Acknowledgements

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8. Kresse, G.; Furthmüller, J. *Phys. Rev.* **1996**, B 54, 11169.

Figure Captions

1. Initial and optimized structures of nitromethane interacting with a four-layer ($\sqrt{7}$x$\sqrt{7}$) R19.1° aluminum (111) slab model.

2. Initial and optimized structures of 1,1-diamino-2,2-dinitroethylene ("FOX-7") interacting with a four-layer (3x3) aluminum (111) slab model.

3. Initial and optimized structures of HMX interacting with a three-layer (4x4) aluminum (111) slab model.
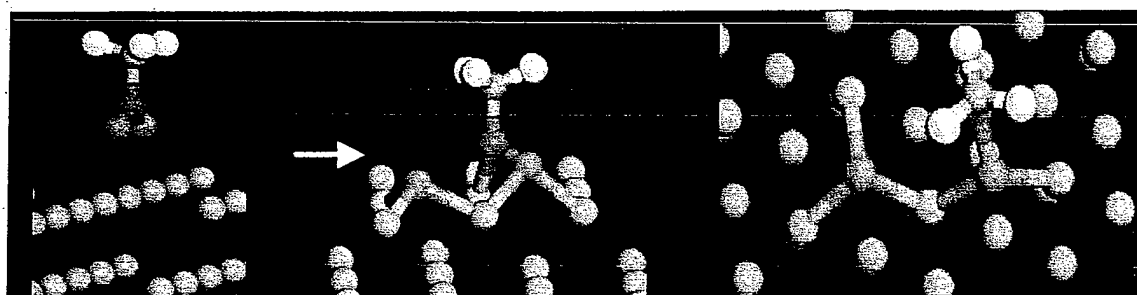
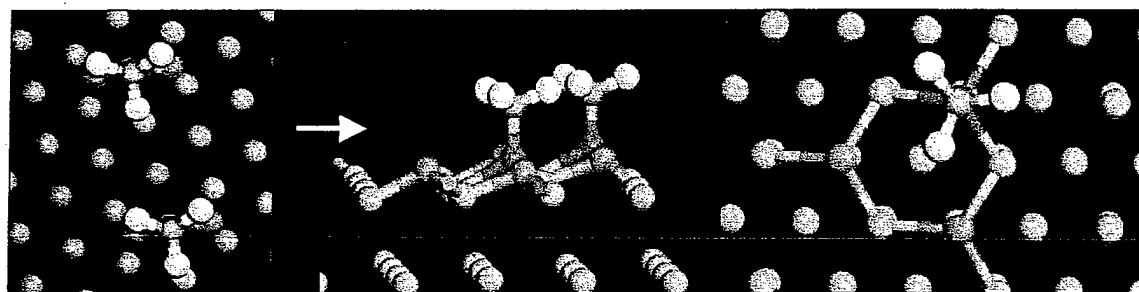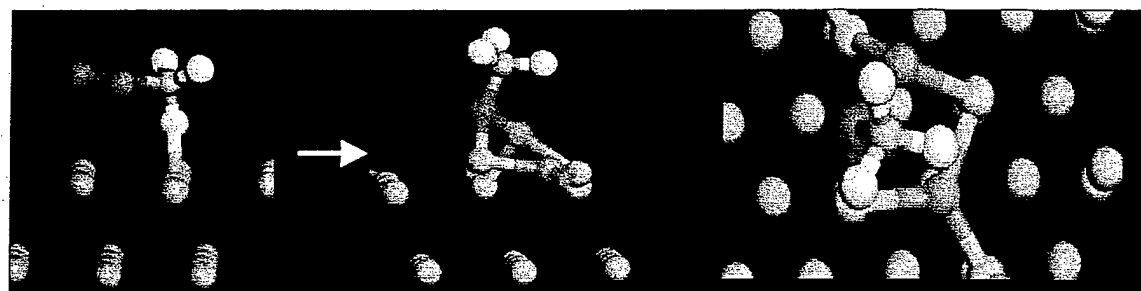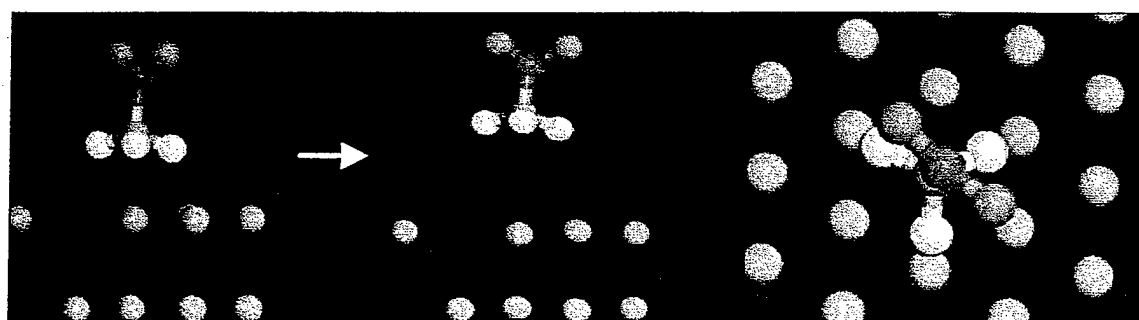| | Initial | Optimized (side view) | Optimized (top view) |
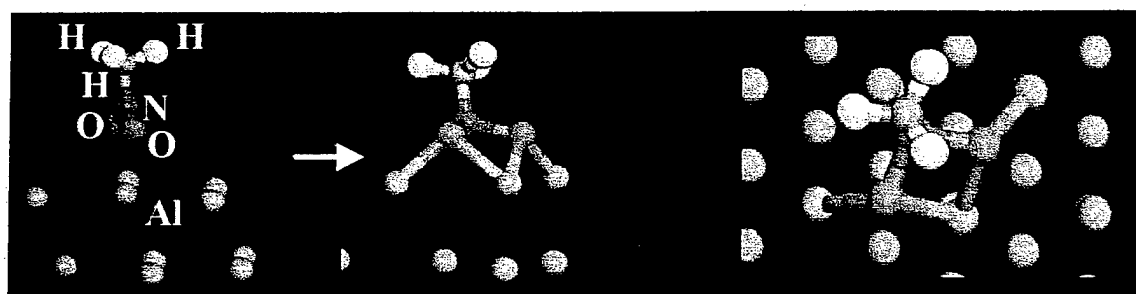
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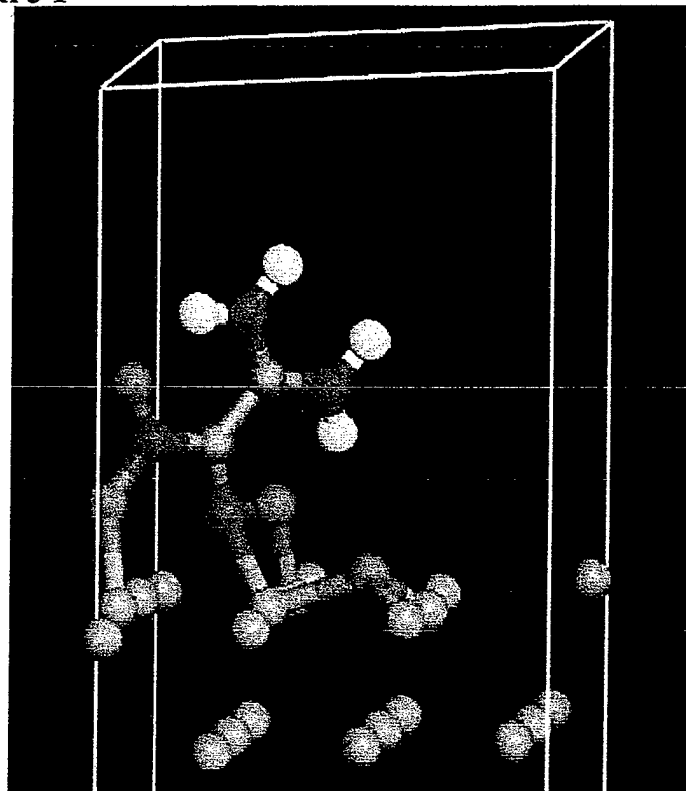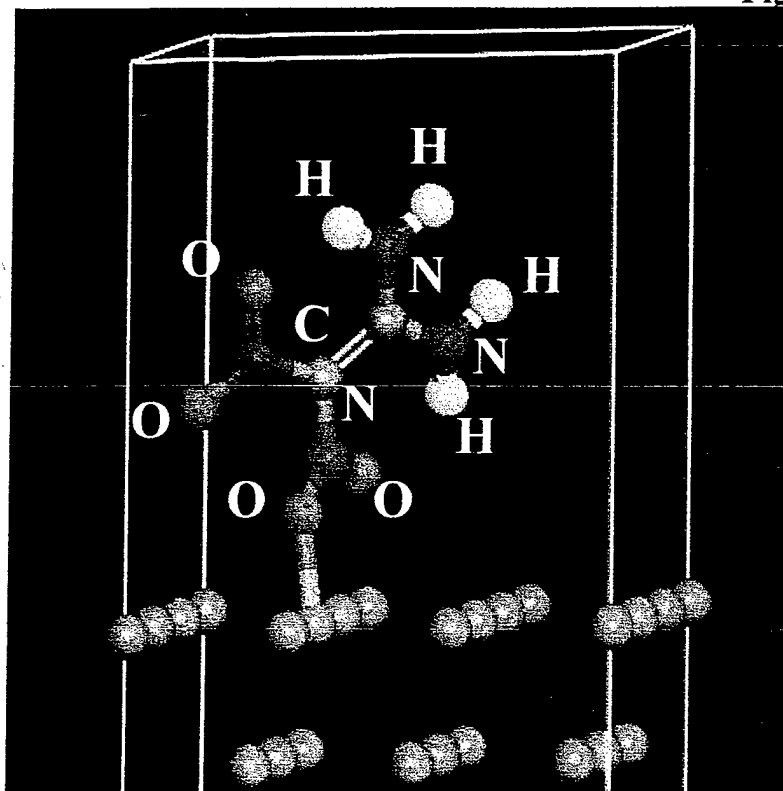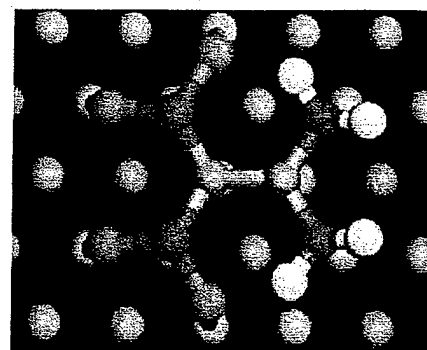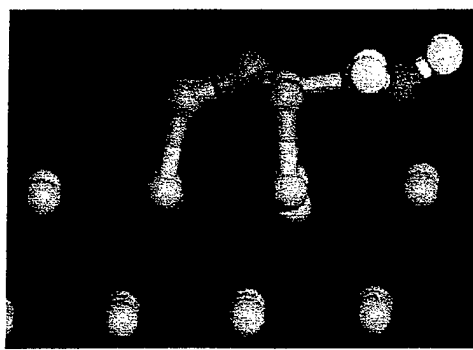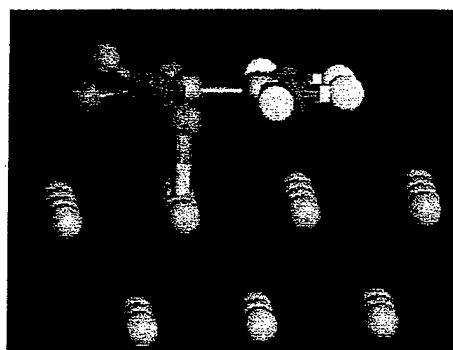
Initial | Optimized

(a)

Initial | Optimized (side view) | Optimized (top view)

(b)

Figure 2
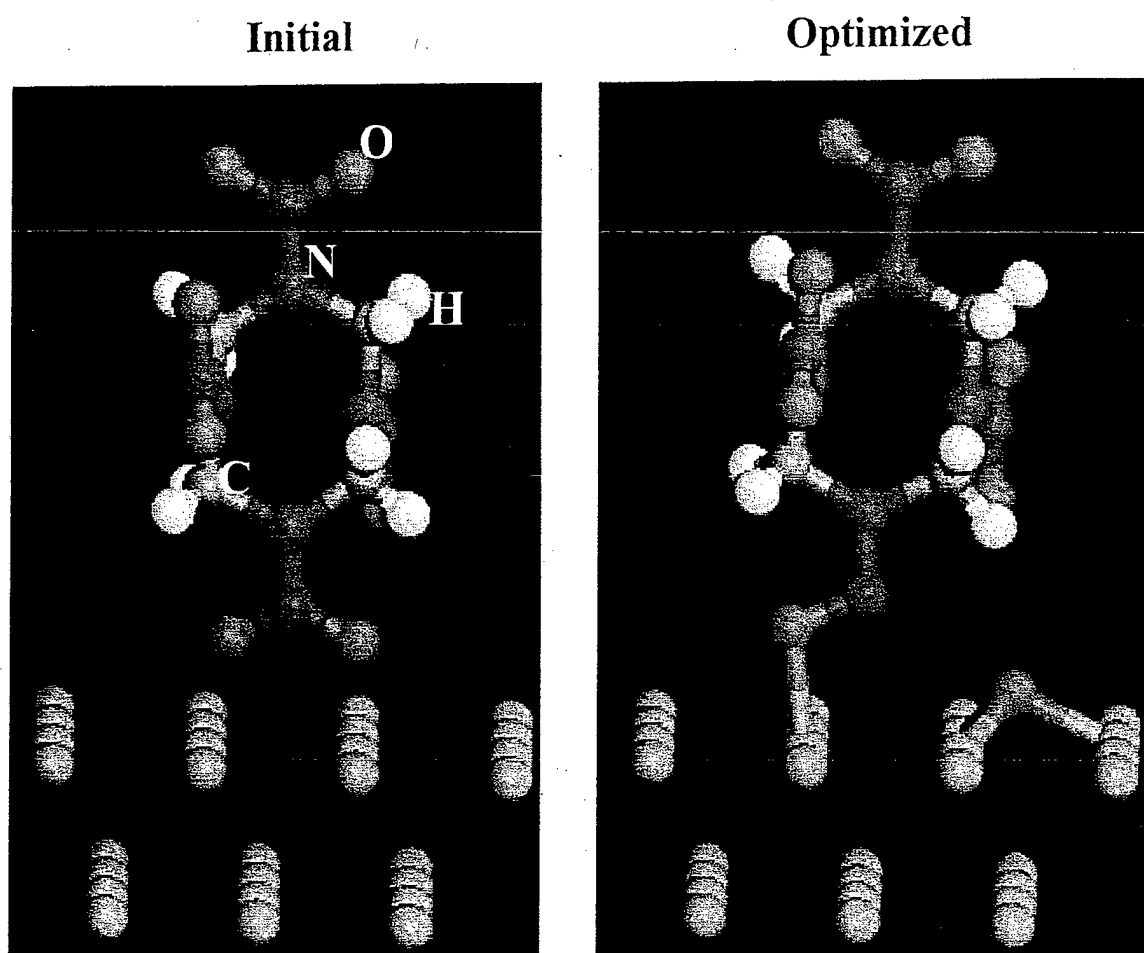
Initial   Optimized

Figure 3